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Effect of alpha-particles irradiation on the phase evolution and chemical stability of Nd-doped zircon ceramics

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ABSTRACT

Zircon, $ZrSiO_4$, has a structure that can incorporate actinides. Therefore, the susceptibility of the zircon structure to irradiation damage has been investigated by accelerated irradiation experiments. Synthetic $Zr_{1-x}Nd_xSiO_{4-x/2}$ ($x = 0$, 0.01, 0.10) ceramics were irradiated with 0.5 MeV $^4He^{2+}$ ions (fluences 1×10^{14} -1×10^{17} ions/cm^2) at room temperature. The irradiation effects on phase structure and chemical stability of the ceramics were investigated. It is found that the main crystal structure is maintained, however, little amorphization is leaded as a result of intensified irradiation. Raman spectra reveal that the main peaks slightly broaden and weakened with increasing fluence, indicating little amorphization has been induced by irradiation. The irradiation resistance is enhanced by the growing neodymium content. Moreover, microtopography and element distribution have no changed even after irradiation. Although the LR_{Nd} increases slightly with increasing Nd loading and irradiation, the excellent chemical stability (~10^{-4} g m^{-2} d^{-1}) is maintained.

1. Introduction

Immobilization of long-lived actinides from high level nuclear wastes (HLW) into durable crystalline phases is an essential strategy to isolate actinides from the biosphere [1–5]. Ceramic has been employed for nuclear waste immobilization for more than sixty years due to its good long term stability, although it present some disadvantages related to the high processing temperature. The alpha-decay of the immobilized actinides can affect the physical-chemical properties of waste forms in long term geologic storage [6]. In alpha decay of actinides, a high energy alpha particle (~4–6 MeV), an energetic recoil nucleus (~0.1 MeV), and gamma radiation are released [7]. The gamma radiation generally results in negligible damage relative to the alpha particle and the recoil nucleus. Nearly all the energy of the recoil nucleus is lost through elastic collisions with atoms in the structure, producing highly localized damage (displacement cascade) with one to two thousand atomic displacements. The alpha particle, on the other hand, dissipates most of its energy by ionization processes, but still undergoes enough elastic collisions along its path to produce several hundred isolated atomic displacements. Therefore, it is very necessary to evaluate the effect of alpha-irradiation on the actinide-bearing crystalline ceramics.

Zircon ($ZrSiO_4$, tetragonal space group $I4_1/amd$) under consideration in this study has long been recognized as a waste forms material for the immobilization of high-level nuclear waste [8–10]. Up to now, numerous works have been focused on the investigation of phase evolution or immobilization capacity of zircon by actinides substitution for Zr in $ZrSiO_4$ structure. Hence, compositions of $ASiO_4$, in which A^{4+} = Zr, Hf, Th, Pa, U, Np, Pu, Am, Ce and Nd, have been synthesized [11–15]. Previous works demonstrate that zircon structure has good immobilization capacity for actinides. Given that nuclear waste forms will be subject to considerable α-recoil irradiation damage in geological repository, it is important to understand effect of α-irradiation on the synthetic zircon ceramics waste forms. Up to now, some works have been devoted to investigate the irradiation induced structure modification in nature zircon [16–20]. For instance, Nasdala et al. [21] found that the irradiation damage haloes generated by alpha particles in nature zircon. Nature and synthetic zircon were irradiated with 8.8 MeV $^4He^{2+}$ ions at fluencies ranging from 1×10^{13} to 5×10^{16} ions/cm^2

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[22]. This ion energy is equivalent to the highest of the common alpha energies in the natural U and Th decay chains (i.e. alpha particles produced in the $^{212}Po \rightarrow {}^{208}Pb$ decay within the ^{232}Th chain). Trachenko et al. [23] investigated the effects of simulating high-energy recoils irradiation damage on structural changes in zircon. The effects of self-irradiation damage as a function of cumulative alpha-decay events in synthetic zircon doped with ^{238}Pu and natural zircons damaged over geologic time were compared and interpreted in terms of the accumulation of both defects and amorphousness [24]. Irradiation damage of natural and synthetic zircon grains was evaluated by Raman spectroscopy to understand annealing and stability of fission tracks [25]. Furthermore, Barrera-Villatoro et al. [26] investigated the cathodoluminescence response of natural and synthetic lanthanide-rich phosphates (Ln^{3+}: Ce, Nd). As noted above, the irradiation performance of zircon (mainly nature zircon) has been investigated. However, to the best of our knowledge, the information about the irradiation effects of synthetic zircon ceramics waste forms is not well understood. And they mainly focused on the effects of the irradiation energy and fluence on the structure modification. The effects of immobilized actinides content and phase structure on the irradiation performance of ceramics waste forms have not been investigated systematically. In our previous work [14], we prepared $Zr_{1-x}Nd_xSiO_{4-x/2}$ ($0 \leq x \leq 0.1$) ceramics waste forms by solid-state reaction method. The effects of neodymium (Nd) content on the phase structure of the zircon ceramics were investigated. It was found that the ceramics with $x < 0.04$ show homogeneous single zircon phase, while the samples with $x \geq 0.04$ exhibit coexistence of two crystal phases (zircon and $Nd_2Si_2O_7$). Moreover, the bulk density of the Nd-doped zircon ceramics increases with increasing neodymium content. However, the susceptibility of the Nd-doped zircon ceramics to irradiation damage has not been investigated. Particularly, question of whether irradiation damage may modify the phase, microstructure and chemical stability of the Nd-doped zircon ceramics has never been addressed. Moreover, how the Nd content and the formation of second phase ($Nd_2Si_2O_7$) affect the irradiation resistance of zircon ceramics waste forms?

Therefore, based on our previous works, the motivation of this work was to explore the irradiation tolerance of composites $Zr_{1-x}Nd_xSiO_{4-x/2}$(x = 0, 0.01, 0.10) with different Nd content and phases. Alpha-particles irradiation was conducted considering the alpha-decay of actinides in the long term geologic storage. In order to evaluate the irradiation performance of these ceramics waste forms, Gracing Incidence X-ray Diffraction (GIXRD) was employed to investigate their phase and microstructure modification as a function of Nd content and irradiation fluences, Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM/EDX) were performed to distinguish the micro-morphology and element distribution evolutions under alpha-particles irradiation, and Raman spectra was collected to get the detailed local information of the irradiated samples.

2. Experimental

2.1. Nd-doped zircon waste forms fabrication

In the experiments presented in this paper, we selected neodymium (Nd) as potential surrogate for the trivalent actinides [27,28]. The choice is based on three criteria: the possible valence of the candidate elements, the ionic radii for a given coordination number, and the electronic configuration. According to the theory of isomorphism, we speculated the Zr of $ZrSiO_4$ structure can be substituted by Nd. Moreover, considering the ions charge balance, the chemical general formula $Zr_{1-x}Nd_xSiO_{4-x/2}$ is employed.

ZrO_2 (Aladdin Chemistry Co. Ltd., Shanghai, China, purity of 99.99%), Nd_2O_3 (Aladdin Chemistry Co. Ltd., Shanghai, China, purity of 99.99%) and SiO_2 (Chengdu KESHI Chemical, purity of 99.9%) were used as raw materials. Series of compositions with general stoichiometry as $Zr_{1-x}Nd_xSiO_{4-x/2}$ (x = 0, 0.01, 0.10) were obtained by solid state reaction method. Before use, all the raw materials were heated at 120 °C over night to remove the possible moisture. Then stoichiometric amounts of the powders were weighed, and ground/mixed in ethyl alcohol medium (purity of 99.7%, the mass ratio of ethyl alcohol to powder was about 3:1) by ball milling. The powders were dried again and then pressed into pellets of 12 mm in diameter and 0.5 mm in thickness at a pressure of 10 MPa. The pellets were sintered at 1550 °C for 72 h to fabricate dense bulk ceramics in air atmosphere. The heating rates were about 5 °C per minute in the sintering steps. More preparation details are displayed in our previous work [14].

2.2. Alpha-irradiation

The alpha irradiation experiment was performed using a 320 KV multi-discipline research platform for highly charged ions at the Institute of Modern Physics, Chinese Academy of Sciences. The 0.5 MeV alpha-particles were implanted at fluences ranging from 1×10^{14} to 1×10^{17} ions/cm^2, which was achieved by varying the exposure times to the beam between 9 and 8700 s. The beam was focused to a rectangular area of about 1.6 × 1.7 cm^2 size. Samples were irradiated at room temperature.

2.3. Leaching experiments

We used the static leach test (Materials Characterization Center, MCC-1) method to obtain the leaching rates of each Nd-doped zircon waste forms. The synthetic Nd-doped zircon ceramics was hanged in a 100 ml Teflon-lined pressure vessel, which was then placed in the deionized water in a stainless steel vessel, sealed and then heated in an oven for certain time. Leaching test of the waste forms was performed in a hydrothermal reaction device using the MCC-1 at 40 °C at regular intervals (1, 3, 7, 14, 21, 28, 35 and 42 days). The ionic concentration (C_i) of Nd in the solution was analyzed with an inductively coupled plasma mass spectrometer (ICP-Mass, Agilent 7700x, Agilent, U. S.).

The normalized release rate (LR_i, g m^{-2} d^{-1}) of each element was calculated as the following equation:

$$LR_i = \frac{C_i \cdot V}{S \cdot f_i \cdot t_n} \quad (1)$$

Where C_i is the concentration of element i in the solution (g/m^3), V is the volume of the leachate (m^3), S is the surface area of ceramics (m^2), t_n is the leaching time (d) and f_i is the mass fraction of element i in ceramics (wt.%).

2.4. Characterization

The phase structures of the Nd-doped zircon ceramics were characterized by powder X-ray diffraction (XRD, X'Pert PRO, PANalytical B. V, Netherlands) with Cu-Kα (λ = 1.5406 Å) irradiation, over the two theta range of 10–80° with step width and time of 0.02° and 1.2 s, respectively. Grazing incidence X-ray diffraction (GIXRD) was performed on a Netherlands Panalytical X-ray diffractometer with Cu-Kα irradiation, and θ-2θ geometry. The step size of the scan angle was 0.02°, and the scan range was 10–80° under X-ray incident angles from 0.5° to 10°. The microstructure of the sintered samples was observed by scanning electron microscope (SEM, Ultra 55, Germany). The element distribution was